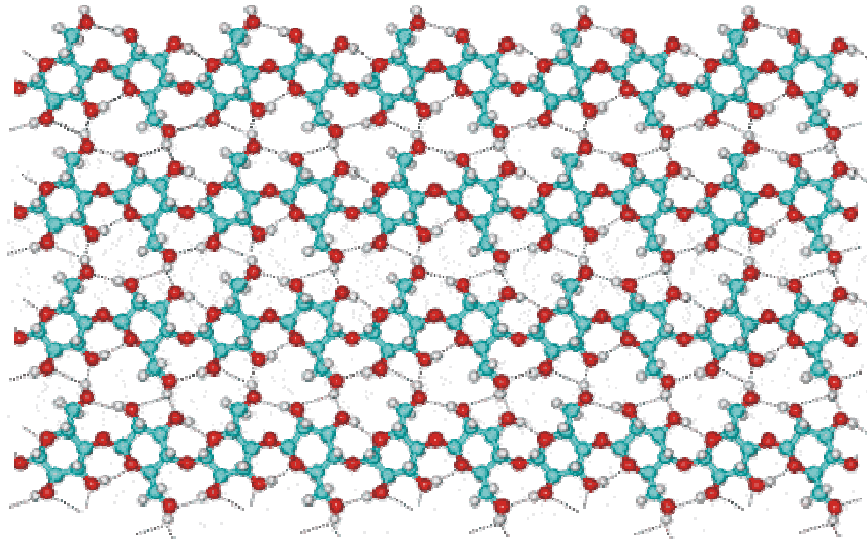
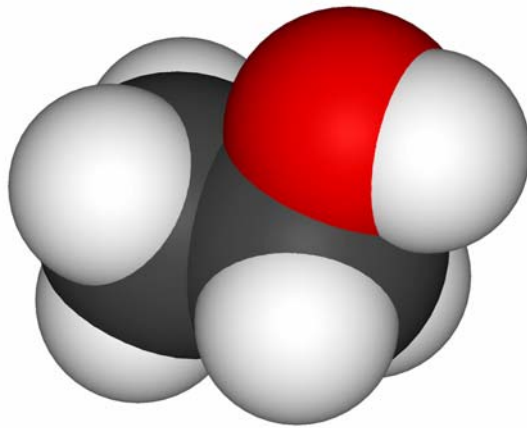


Cellulosic Biofuel Technologies

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Cellulose



Ethanol

Cellulosic Biofuel Technologies

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EXECUTIVE SUMMARY

The United States imports 60% of its petroleum. This contributes substantially to the country's negative balance of payments. Half of the imported petroleum (30% of total consumption) comes from unstable parts of the world. Domestically produced biofuels could replace the petroleum imported from these unreliable sources, thus reducing dependence on foreign oil and increasing national energy security.

Biofuels currently produced in the United States are primarily ethanol from corn and biodiesel from soybeans. Increased demand for these grains by the burgeoning grain-based biofuel industry is driving grain prices up and creating considerable concern about the potential negative impacts on a wide range of food products that depend on grain: chicken, pork, beef, and dairy products such as milk, cheese, yoghurt, cream and ice-cream. Consequently, development and commercialization of technologies to produce biofuels from cellulosic materials such as wood, grasses, crop residues and animal waste deserves urgent attention, and the objective of this study was to identify and evaluate technologies for production of cellulosic biofuels.

Information for this report was obtained from literature and web searches, attending conferences, visiting government agencies and private companies, and conducting informal interviews. In some cases it was necessary to sign non-disclosure agreements, which precluded publishing information from the associated entities. However, considerable valuable insights were obtained from these confidential sources.

The key findings of this study were:

- 1) Considerable activity in developing and commercializing cellulosic biofuel technologies is occurring under cover, in the private sector, and this includes some of the most promising processes.
- 2) Besides technologies to produce cellulosic ethanol, procedures are also being developed to produce cellulosic diesel (not biodiesel, from vegetable oil), cellulosic gasoline, and cellulosic aviation fuel.
- 3) For production of cellulosic ethanol, gasification and catalytic conversion (the thermochemical route) appears to offer greater promise than acid or enzyme hydrolysis followed by fermentation (the biochemical route).
- 4) Production of cellulosic diesel, gasoline and aviation fuel by depolymerization and catalytic synthesis has received relatively little attention, but appears to be superior to all other technologies.

INTRODUCTION

The United States is responsible for 25% of world oil consumption but owns only 3% of global oil reserves. The country imports about 60 percent of the crude oil it consumes, and approximately half of this (30%) comes from unstable parts of the world (the Middle East, Venezuela and Nigeria, Table 1). Along with prolonged war in Iraq and gasoline price shocks in response to reduced global supply and damage to Gulf Coast oil refineries by hurricanes (especially Katrina and Rita in 2005), this has emphasized how vulnerable the country is from an energy security point of view. Heightened awareness of the role fossil fuels play in aggravating the risk of climate change and the need to stimulate rural economies are further incentives for exploring alternative domestic sources of energy.

Table 1. Sources of imported oil (adapted from Manternach, 2004).

| <u>Source</u> | <u>% of National Consumption</u> |
|---------------------|----------------------------------|
| Canada | 10.4 |
| Mexico | 10.3 |
| Mid East | 14.6 |
| Saudi Arabia | (9.3) |
| Iraq | (4.1) |
| Kuwait | (1.2) |
| Venezuela | 8.7 |
| Nigeria | 7.1 |
| Other | <u>9.9</u> |
| TOTAL | <u>60.0</u> |

Collectively, these factors have spurred unprecedented interest in biofuels in both the public and private sectors. Annual consumption of gasoline in the U.S. is about 140 billion gallons and annual diesel consumption is about 40 billion gallons, amounting to a total of 180 billion gallons a year. In 2006 it is expected that approximately 5 billion gallons (3% of national gasoline consumption) of fuel grade ethanol will be produced from corn grain. At this time there are about 100 corn-to-ethanol plants in commercial production, and approximately 40 under construction. It is expected that ethanol from corn grain could possibly be expanded to around 15 billion gallons a year, after which further expansion will likely increase the price of corn sharply, along with that of associated food products such as chicken, pork, beef and milk.

In view of this situation, alternatives to ethanol produced from corn are urgently needed. In the short term, cellulosic ethanol, which is ethanol produced from cellulosic, ligno-cellulosic or fibrous biomass/plant material (as opposed to raw materials with

high sugar contents, such as sucrose in sugarcane and sugar beet, or high concentrations of starch, like corn grain and sweet potatoes) appears to be the best option.

While research on technologies to produce cellulosic ethanol has been in progress for decades, there appear to be no known plants in the world that produce cellulosic ethanol commercially. However, starting at the beginning of 2006 there has been a sharp increase in attempts to achieve this goal. On January 31 of 2006 President Bush indicated in his State of the Union Address that “We will also fund additional research on cutting-edge methods of producing ethanol, not just from corn, but from wood chips, and stalks, and switchgrass. Our goal is to make this new kind of ethanol practical and competitive within six years”.

On a visit to Hoover, Alabama, on September 28, 2006, for a briefing on E-85 (a blend of 85% ethanol and 15% gasoline) and cellulosic ethanol the President made the following comment to the press: “You know, the price of gasoline has been dropping, and that's good news for the American consumer, it's good news for the small business owners, it's good news for the farmers. But it's very important for us to remember that we still have an issue when it comes to dependence on foreign oil. And one way to become less dependent on foreign oil is for us to develop new ways to power our automobiles right here in America”

(<http://www.whitehouse.gov/news/releases/2006/09/20060928-3.html>)

Just a few weeks later he repeated this sentiment at the “Advancing Renewable Energy” conference in Saint Louis hosted by the Secretaries of Agriculture and Energy, adding the following: “And in my judgment, the thing that's preventing ethanol from becoming more widespread across the country is the lack of other types of feedstocks that are required to make ethanol -- sugar works, corn works, and it seems like it makes sense to spend money, your money, on researching cellulosic ethanol, so that we could use wood chips, or switchgrass, or other natural materials. And we've got an aggressive effort to research new raw materials to be used in ethanol. It makes a lot of sense for the federal government to continue to invest taxpayers' money, because the more different raw materials that are practically in use, the more ethanol production facilities will spread around the country. And the more spread around -- the more production there is, the more likely it is that the entire industry will evolve quicker.”

(<http://www.whitehouse.gov/news/releases/2006/10/20061012-4.html>)

In addition to strong support from the White House, development of cellulosic ethanol is receiving considerable attention from federal agencies, including the DOE, USDA and EPA. In the past two years there have been two major reports released: 1) “Biomass as Feedstock for a Bioenergy and Bioproducts industry: The Technical Feasibility of a Billion-Ton Annual Supply”, April 2005

(http://feedstockreview.ornl.gov/pdf/billion_ton_vision.pdf) and 2) “Breaking the Biological Barriers to Cellulosic Ethanol”, June 2006, (<http://genomicsgtl.energy.gov/biofuels/2005workshop/b2blowres63006.pdf>).



President George W. Bush addressing the press at the Hoover, Alabama, E-85 Fueling Facility, September 28, 2006.



Alabama Governor Bob Riley discusses the merits of E-85 use in the Hoover police fleet with President George Bush, September 28, 2006.

Cellulosic ethanol has also recently attracted the attention of major investors like Vinod Khosla, co-founder of Daisy Systems and founding Chief Executive Officer of Sun Microsystems, and Sir Richard Branson of the Virgin Group who has pledged \$3 billion towards development of renewable fuels. In a recent article in Wired Magazine (<http://www.wired.com/wired/archive/14.10/ethanol.html?pg=1> , 2006) Khosla makes a convincing case for cellulosic ethanol, although he concedes that other fuels like butanol could play a role in the future. In this article he provides strong arguments to refute six ethanol myths:

1. It takes more energy to make ethanol than the fuel itself produces.
2. Ethanol is expensive to produce.
3. There's not enough land to grow crops to produce ethanol.
4. Switching to ethanol is expensive.
5. Ethanol is unfairly subsidized.
6. Cars that run on ethanol get lower mileage.

He predicts that by 2012 cellulosic ethanol will be commercial and by 2022, along with other “biohols”, it will contribute substantially to meeting the demand for transportation fuels (Figure 1).

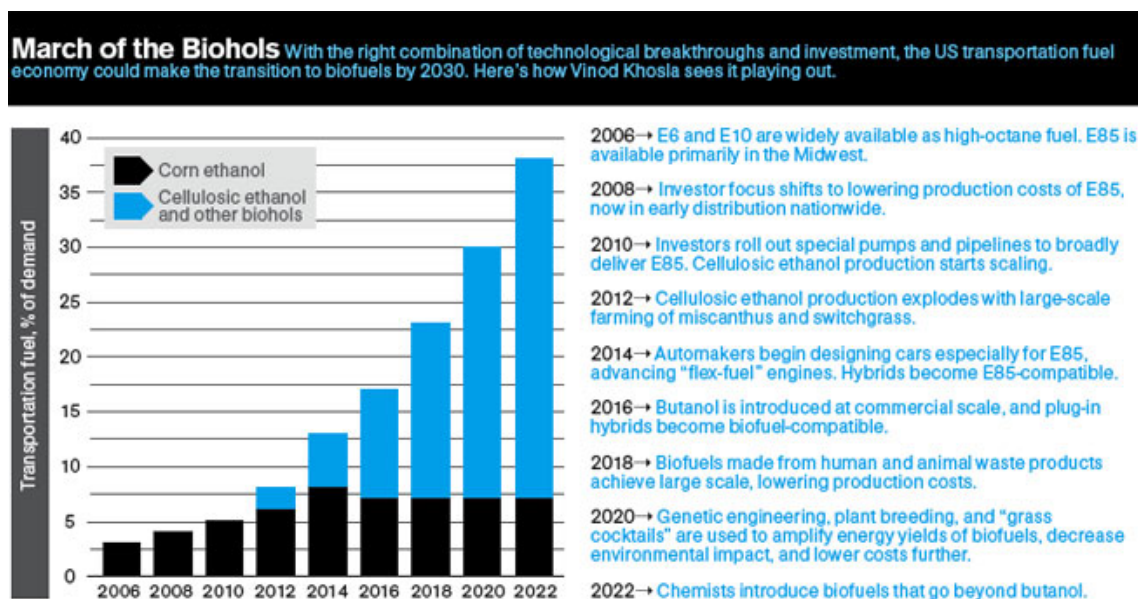


Figure 1. Vinod Khosla's predicted change in the role of cellulosic ethanol and other biohols over time (Source: Wired Magazine, October, 2006).

Potential of using hydrogen as a transportation fuel is considered by some as competition to development of cellulosic ethanol. However, in his publication “A better way to get from here to there” (<http://www.newrules.org/electricity/betterway.pdf>) David Morris, vice president of the Institute for Local Self Reliance (ILSR, <http://www.ilsr.org/>) argues that hybrid vehicles and renewable fuels like cellulosic ethanol offer a better alternative. He also provides an opinion on “Putting the pieces together: Commercializing Cellulosic Ethanol”

(<http://www.newrules.org/agri/celluloseethanol.pdf>) and an excellent source on the ethanol energy balance debate (<http://www.newrules.org/agri/netenergy.html>).

Since energy balance is a common issue raised by many citizens, it deserves some comment here. Pimentel and Patzek (<http://petroleum.berkeley.edu/papers/Biofuels/NRRethanol.2005.pdf>) appear to be alone among many authors in their view that the energy balance for ethanol production is negative, or consumes more energy than is contained in the ethanol that is produced. In general, ethanol produced from corn grain has an energy balance of between 1.3 and 1.6 units out as ethanol for each unit of fossil fuel used in the production process. However, as pointed out by Khosla (<http://www.wired.com/wired/archive/14.10/ethanol.html?pg=1>) if the natural gas that is typically used to produce heat for distillation in the corn-to-ethanol process is replaced by biomass, this ratio can be increased dramatically to over 5:1. Because corn is an annual crop that requires considerable mechanical energy for planting each year, the energy balance for ethanol produced from perennial energy crops like switchgrass will almost certainly be considerably higher. Of particular importance, Khosla also points out that contrary to common belief, the energy balance for production of gasoline is negative, at 0.8:1. This is probably also due mainly to the high requirement of natural gas and/or coal in the oil refining process.

Finally, it is very important to recognize that it is possible to produce regular hydrocarbon fuels such as diesel (commonly referred to as synthetic diesel, syn-diesel or cellulosic diesel, but not biodiesel which is produced mostly from vegetable oil) gasoline (synthetic gasoline) and even aviation fuel from cellulosic biomass. For the purpose of this document, these fuels are referred to as cellulosic hydrocarbons or cellulosic hydrocarbon fuels, or cellulosic diesel, gasoline and aviation fuel. Furthermore, because these fuels require no change in distribution infrastructure and automobile engines, as is the case with respect to ethanol, they have a distinct advantage over ethanol.

While cellulosic biofuels offer considerable opportunity to play an important role in the US and global energy future, they will be most effective if integrated into a broad master energy plan. This is brought out strongly by Amory Lovins, Chief Executive Officer of the Rocky Mountain Institute (<http://www.rmi.org/>) in his book “Winning the Oil Endgame” (<http://www.oilendgame.com/>).

In summary, both public and private sector support suggests that the potential role of cellulosic biofuels in meeting the future demand for transportation fuels is good. Therefore, cellulosic biofuels will likely increase national energy security, improve rural economies and reduce risk of global climate change. In view of this, and the fact that several technologies for producing ethanol from ligno-cellulosic material are under development, the objective of this study was to conduct a comparative analysis of emerging cellulosic biofuel technologies to inform potential investors and thus facilitate rapid commercialization.

PROCEDURE

Information for this document was collected by conducting formal literature and web searches, attending conferences, visiting companies that are developing cellulosic biofuel technologies, and conducting personal interviews. Company visits usually required execution of non-disclosure agreements. While this precluded publication of any proprietary details, the visits provided valuable technological insights that are captured in the general technology descriptions.

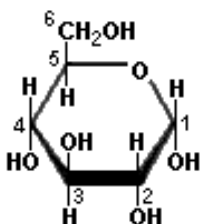
To fully understand the technology analysis presented in this report it is helpful to have a fundamental understanding of the basic chemistry involved. Therefore, the next section provides a simple description of the basic chemical structure of biomass and selected biofuels. Technologies for producing cellulosic ethanol are then described and discussed. Extensive use is made of information available on the DOE Energy Efficiency and Renewable Energy Biomass Program web site (<http://www1.eere.energy.gov/biomass/>) which provides an excellent general overview of the relevant technologies. Sources of information are provided mainly as web links in the text of the report to facilitate rapid and easy access to them. Although very little specific information is provided from individual companies, contact information is provided for most of the companies identified within the different technology categories in the survey.

CHEMICAL STRUCTURE OF CELLULOSIC BIOMASS

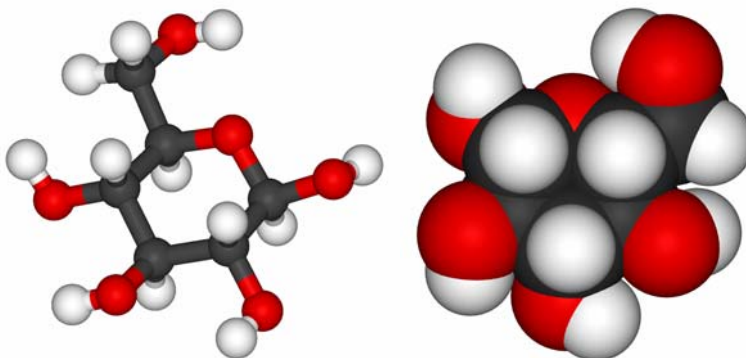
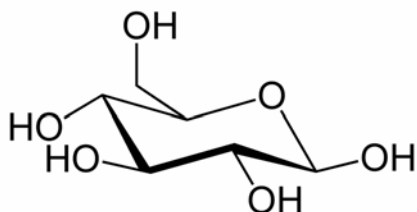
Ligno-cellulosic biomass is carbon-rich material of plant origin. Therefore, along with its biofuel derivatives, it falls into the field of organic chemistry which is essentially the chemistry of carbon. On a dry basis, most biomass contains a little less than 50% carbon by weight. Because the carbon-containing portions of biomass are made up mostly of sugar type molecules, which are carbon rings, biomass can be considered a carbohydrate-based material, whereas fossil fuels are made up of carbon chains and are often referred to as hydrocarbons.

Individual sugars and starch are components of biomass, but not of ligno-cellulosic biomass *per se*. However, because they are the basic building blocks of ligno-cellulosic biomass, and intermediates in the transformation of biomass to ethanol by hydrolysis and fermentation, an understanding of their chemical structure is fundamental to an understanding of the structure of biomass and the technologies used to convert biomass into energy.

Glucose ($C_6H_{12}O_6$) is a simple sugar (or monosaccharide). It is one of the main products of photosynthesis and a component of structural material in plants, thus making it one of the most important carbohydrates in biology. It is a 6-carbon sugar that has several forms, but is typically illustrated as a carbon ring like that indicated below.



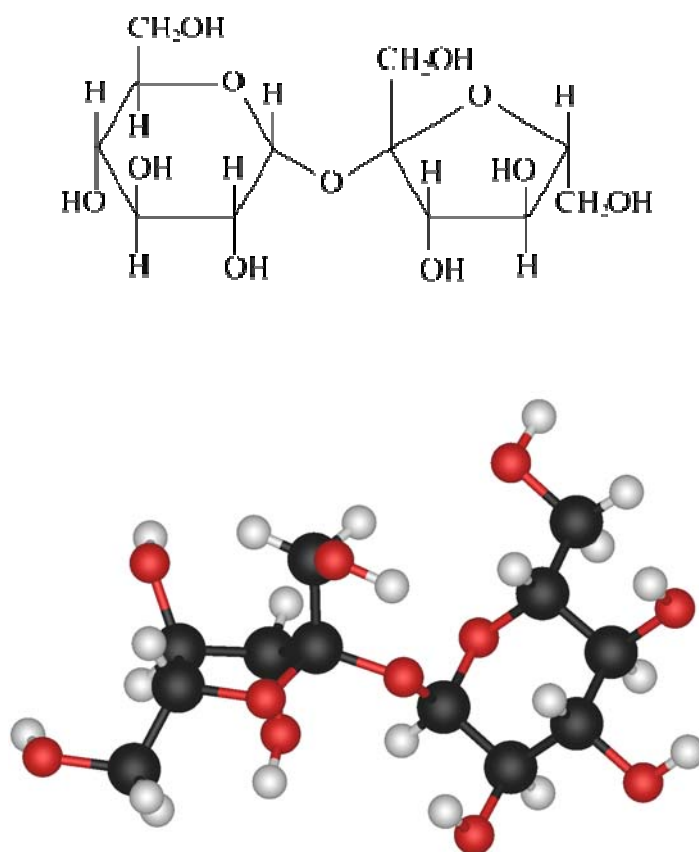
Source: <http://www.scientificpsychic.com/fitness/carbohydrates.html>



Source: <http://en.wikipedia.org/wiki/Glucose>

Figure 2. Several representations of the glucose molecule. (In the color models, black, red and white represent carbon, oxygen and hydrogen, respectively)

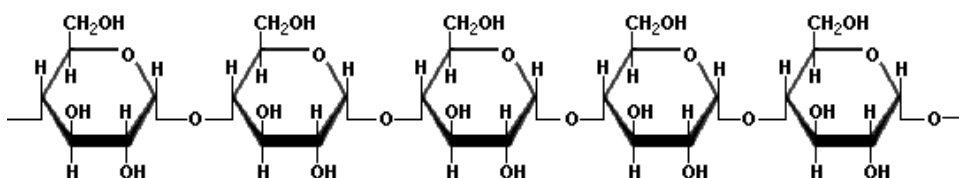
Sucrose ($C_{12}H_{22}O_{11}$) is a disaccharide made up of two simple 6-carbon sugars (glucose and fructose). In its crystalline form it is table sugar, and it is the primary substrate for ethanol produced from sugarcane by fermentation with microorganisms.



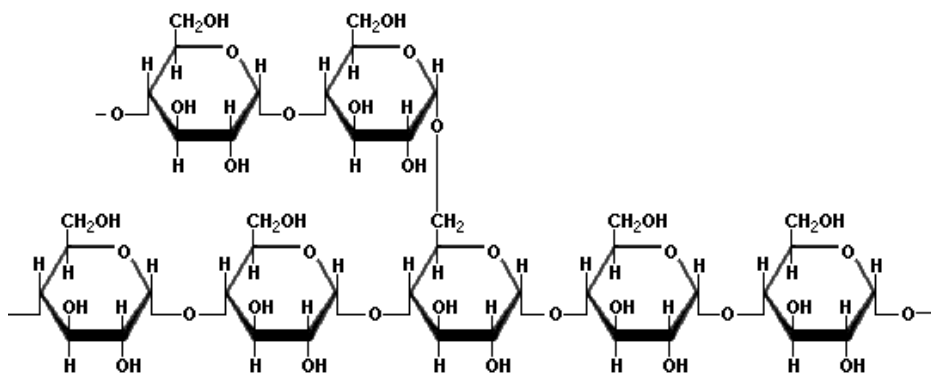
Source: <http://en.wikipedia.org/wiki/Sucrose>

Figure 3. Representation of a sucrose molecule. (In the color models, black, red and white represent carbon, oxygen and hydrogen, respectively)

Starch is a polymer of glucose and the main form of stored carbohydrates in plants. It exists in either linear chains (amylose) or branched chains (amylopectin) of glucose (Figure 4). As a major component of corn grain, it is the primary substrate for ethanol produced from corn. This process involves hydrolysis, or breaking up the starch into individual sugars with enzymes or biological catalysts, and subsequent fermentation of the resultant sugars into ethanol by microorganisms.



Amylose



Amylopectin

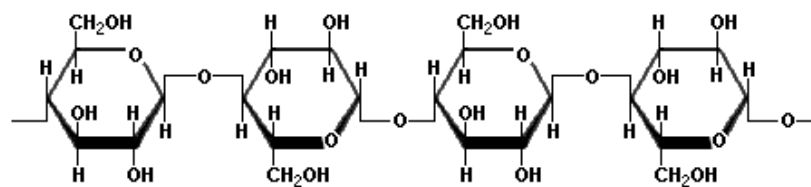


The side branching chains within the amylopectin molecule

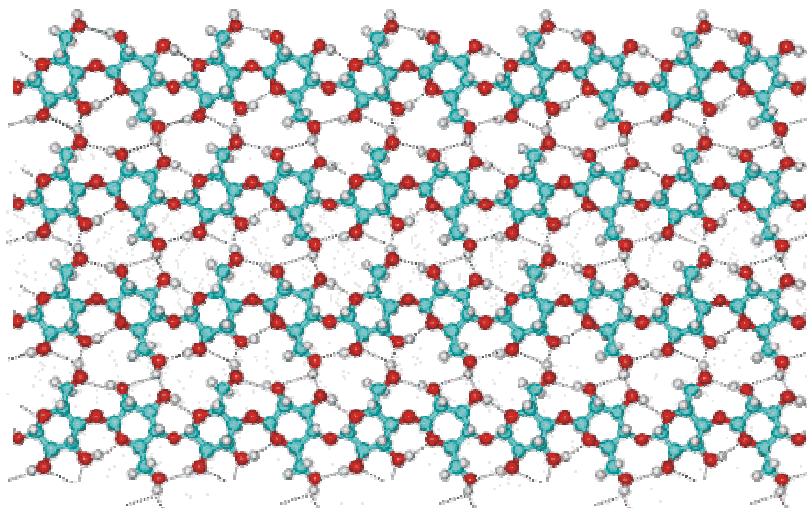
Source: <http://www.scientificpsychic.com/fitness/carbohydrates.html>

Figure 4. Diagram of starch molecules.

Cellulose is also a polymer of glucose, but unlike starch, the chains are unbranched. This allows the molecules to lie close together to form rigid structures. Therefore, cellulose is the major structural carbohydrate in plants. It is the most abundant form of carbon in the biosphere. Wood is mainly cellulose and cotton lint is almost pure cellulose. The cellulose in wood is the primary constituent of pulp for making paper. Cellulose can be hydrolyzed into glucose by enzymes from microorganisms that inhabit the digestive tracts of ruminant animals like cows and goats, and termites. The resultant glucose can then be fermented into ethanol.



Source: <http://www.scientificpsychic.com/fitness/carbohydrates.html>



Source: <http://www.lsbu.ac.uk/water/hycel.html>

Figure 5. Chemical structure of cellulose.

Hemicellulose is similar to cellulose in that it is a polymer of sugars and a structural carbohydrate. However, in contrast to cellulose that is made up of only glucose molecules connected to one another in long, rigid chains, hemicellulose contains a variety of sugars including both 5- and 6- carbon monomers (Figure 6) that are randomly attached to one another. Xylose is one of the 5-carbon sugars and is the second most abundant sugar in the biosphere. Hemicellulose is more easily hydrolyzed into its component sugars, but the resultant 5-carbon sugars are more difficult to ferment into ethanol than glucose.

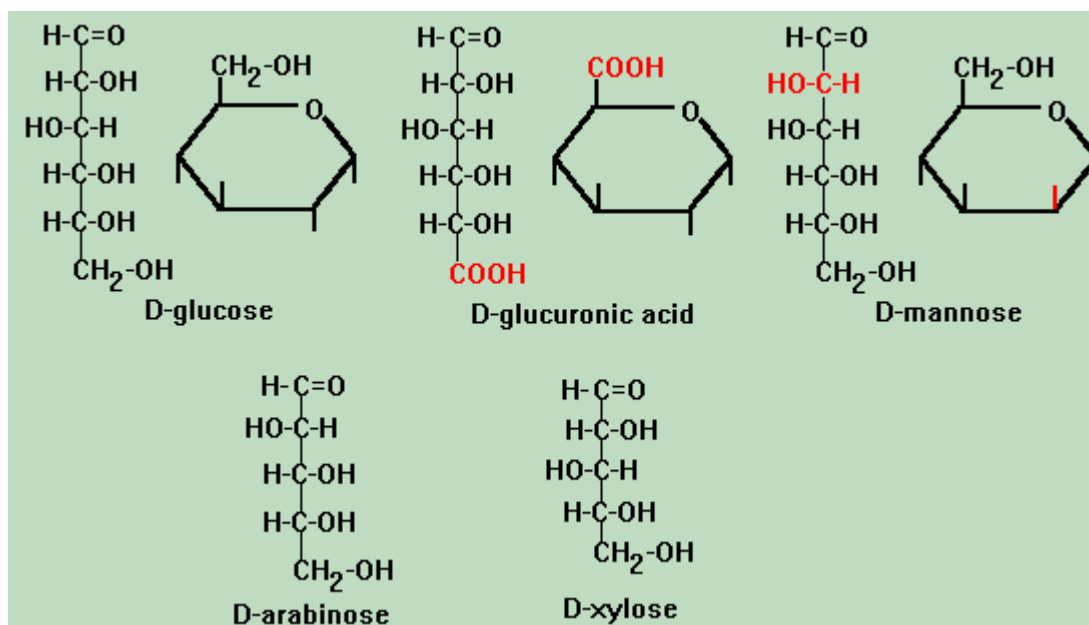


Figure 6. Some of the component sugars of hemicellulose.

Lignin is the toughest structural material in biomass. It is made up of complex molecules (Figure 7) that resist biological breakdown or biochemical conversion. In addition, because it is often very closely aligned with cellulose and hemicellulose, it can limit the hydrolysis of these constituents by blocking access of enzymes to them (<http://genomicsgtl.energy.gov/biofuels/2005workshop/b2blowres63006.pdf>). This phenomenon is sometimes referred to as recalcitrance. Because of its relatively high carbon content compared to cellulose and hemicellulose, lignin has a high energy content.

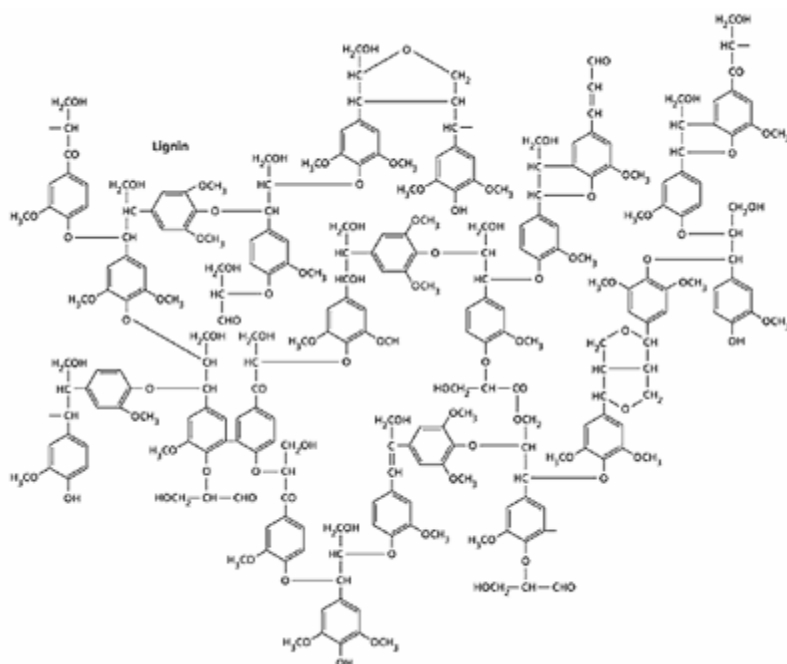


Figure 7. Chemical structure of portion of a lignin molecule.

Ligno-cellulosic biomass is typically made up of 38-50% cellulose, 23-32% hemicellulose and 15-35% lignin. Wood and agricultural legumes are generally higher in lignin and cellulose than grasses, while grass-based biomass like switchgrass and corn stover is typically higher in hemicellulose, although there are exceptions to this general pattern (Table 2).

Table 2. Cellulose, hemicellulose and lignin content of selected ligno-cellulosic biomass materials

| <u>Biomass Material</u> | <u>Ash</u> | <u>Cellulose</u> | <u>Hemicellulose</u> | <u>Lignin</u> |
|--------------------------------|-------------------|-------------------------|-----------------------------|----------------------|
| Corn stover | 11.04 | 30.61 | 19.13 | 18.19 |
| Sugarcane bagasse | 4.04 | 42.64 | 25.40 | 24.05 |
| Switchgrass | 5.76 | 30.97 | 24.35 | 17.56 |
| Wheat straw | 10.22. | 32.64 | 22.63 | 16.85 |
| Poplar (whole tree) | 1.94 | 41.13 | 18.01 | 28.05 |

CHEMICAL STRUCTURE OF SELECTED LIQUID FUELS

Fossil fuels are often referred to as hydrocarbons because they are composed of carbon chains (as opposed to chains of carbon rings, as in biomass) with mainly hydrogen attached. Because carbon bonds contain more energy than most other bonds, the more carbon contained in a fuel, the more energy it will contain. This is why butanol contains more energy than ethanol, which is one of the arguments for developing butanol as an alternative transportation fuel to ethanol.

Ethanol can be produced by fermentation of sugars, which is the conversion of sugars to alcohol usually by yeasts ($C_6H_{12}O_6 \Rightarrow 2CO_2 + 2C_2H_5OH$). It is the alcohol component of most alcoholic beverages. For this reason the government requires ethanol intended for use as a transportation fuel to be denatured by addition of a poisonous liquid such as gasoline. Combustion of ethanol is essentially destruction of the ethanol molecule in the presence of heat, oxidation (adding oxygen from the air) of resultant hydrogen into water vapor (H_2O) and carbon into carbon dioxide (CO_2) and the release of energy. Likewise, products of combustion of biomass in an open fire are also water vapor and carbon dioxide which are released into the atmosphere, and ash that remains on the ground.

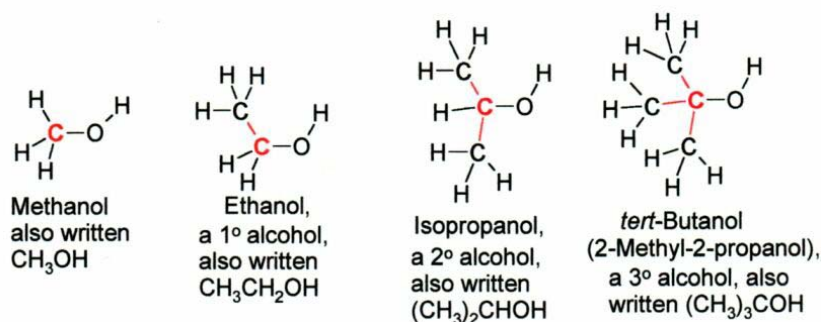


Figure 8. Chemical structure of selected liquid fuels

Source: (<http://en.wikipedia.org/wiki/Alcohol>)

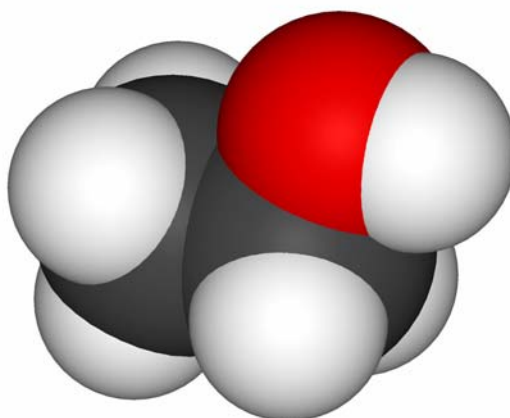


Figure 9. Three dimensional chemical structure of ethanol

Source: (<http://en.wikipedia.org/wiki/Ethanol>)

Hydrocarbon fuels are composed of multiple compounds (not just one) which have a range in length of the carbon chains in their constituent molecules and in some cases they also contain carbon rings. Gasoline typically contains molecules that range between 5- and 12-carbon chains, while diesel molecules mostly contain 12- to 21-carbon chains. In part, this explains why gasoline contains less energy (about 124,000 Btu/gal) than diesel (about 139,000 Btu/gal). Aviation fuel contains intermediate carbon chain lengths (14- to 19-carbon chains) with a slightly different chemical structure that facilitates a cleaner burn than diesel.

CELLULOSIC ETHANOL TECHNOLOGIES

Cellulosic ethanol technologies can be divided into two main categories: biochemical and thermochemical. However, there are a considerable number of process variations within each of these categories. Therefore, the Office of the Biomass Program within the Energy Efficiency and Renewable Energy office of the US DOE refers to the biochemical technologies as the sugar platform, and the thermochemical technologies as the thermochemical platform (Figure 10).

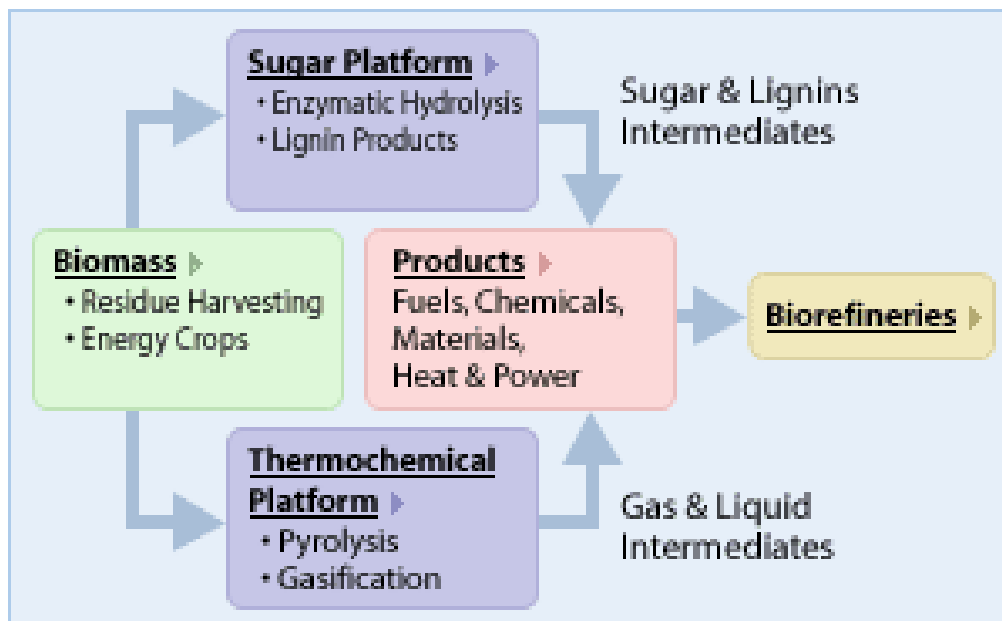


Figure 10. The biochemical (sugar platform) and thermochemical conversion technologies (thermochemical platform) for processing ligno-cellulosic biomass
(Source: US DOE, <http://www1.eere.energy.gov/biomass/>)

Biochemical Technologies

Biochemical technologies for production of cellulosic ethanol involve hydrolysis (break down) of mostly the hemicellulose and cellulose fractions of the biomass into

their component sugars, fermentation of the resultant sugars into ethanol, and concentration or purification of the ethanol by distillation. The hydrolysis step is often preceded by a pretreatment step to break up lignin and more readily facilitate the hydrolysis of hemicellulose and cellulose fractions.

The three primary forms of the biochemical process differ mainly with respect to the hydrolysis step: 1) dilute acid hydrolysis, 2) concentrated acid hydrolysis, and 3) enzymatic hydrolysis. The fermentation step can be essentially the same for all three methods of hydrolysis, but may vary with respect to fermentation organism. Residual, unhydrolyzed cellulose and lignin solids left after hydrolysis are recovered, dried and burned to provide heat or used as a boiler fuel for production steam to drive steam turbines that generate electrical power. However, there appears to be considerable yet largely unexplored opportunity to generate higher value products from this material.

1) Dilute acid hydrolysis

A full description of the dilute acid hydrolysis process is provided at http://www1.eere.energy.gov/biomass/dilute_acid.html. It is the oldest process for producing ethanol from biomass, and involves two stages. The first stage is operated under milder conditions than the second, to optimize hydrolysis of hemicellulose to sugars. The second phase is optimized for hydrolysis of the more resistant cellulose. Resultant sugars are fermented into ethanol and residual unhydrolyzed cellulose and lignin remaining in the hydrolysis reactors are used as boiler fuel to produce steam or electricity. This system is illustrated schematically in Figure 11.

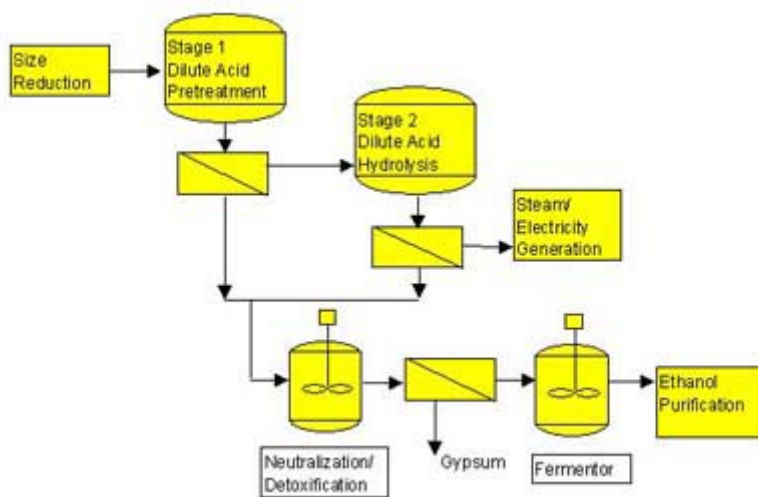


Figure 11. A schematic representation of the dilute acid process.
(Source: http://www1.eere.energy.gov/biomass/dilute_acid.html)

2) Concentrated acid hydrolysis

In contrast with use of only dilute sulfuric acid in the process described previously, concentrated acid hydrolysis (http://www1.eere.energy.gov/biomass/concentrated_acid.html) involves decrystallization of cellulose with concentrated sulfuric acid, followed by hydrolysis to sugars with dilute acid. Major challenges in this process include separation of sugars from acid, recovery of acid, and reconcentration of acid. This process is illustrated schematically in Figure 12.

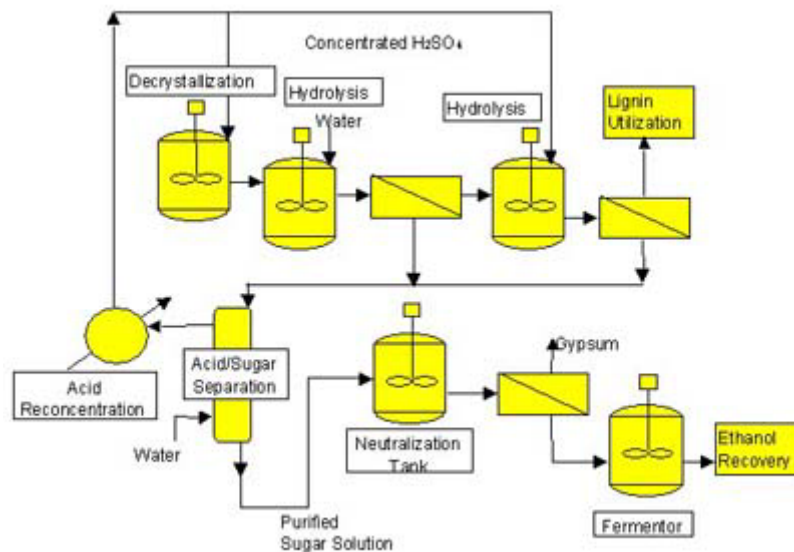


Figure 12. A schematic representation of the concentrated acid process.

(Source: http://www1.eere.energy.gov/biomass/concentrated_acid.html)

3) Enzymatic hydrolysis

Initial attempts to use enzymes (biological catalysts) to hydrolyze cellulose (http://www1.eere.energy.gov/biomass/enzymatic_hydrolysis.html) simply involved replacement of the cellulose acid hydrolysis step. This is known as separate hydrolysis and fermentation. However, because enzymes do not create the harsh environment for microorganisms that acids do, they facilitate a process known as simultaneous saccharification and fermentation (SSF). In this process the cellulase enzyme and fermentation microorganisms are combined, so as sugars are produced by the action of the cellulase they can be immediately converted to ethanol. Consequently, SSF resulted in more rapid throughput, which in turn, improved economic viability.

A major limitation to the economic viability of this process is the high cost of enzyme production. Notwithstanding the improvement in efficiency as a result of

developing SSF and a substantial reduction in the cost of producing enzymes, further improvements in these two factors are still needed. In addition, because enzyme activity varies widely with different feedstocks, considerable work is needed to develop enzymes that can be used in mixtures that will be effective in processing a wide range of feedstocks.

Fermentation

Following hydrolysis, fermentation of resultant sugars to ethanol is the next step which is accomplished in a fermentation tank with the simultaneous release of carbon dioxide (http://www1.eere.energy.gov/biomass/biological_conversion.html). However, in contrast to fermentation of the glucose derived from starch in the corn-to-ethanol process (which can be achieved with inexpensive brewer's yeast) hydrolysis of especially 5-carbon sugars derived from hydrolysis of hemicellulose is difficult. Nevertheless, progress is being made in genetically engineering both yeasts and bacteria that can ferment both 5- and 6-carbon sugars to ethanol. In addition, microorganisms are also being genetically engineered to tolerate harsh conditions (such as elevated temperatures, high salt concentrations and low pH) induced by biomass hydrolyzates, and inhibitors associated with specific feedstocks.

Pretreatment

The term "pretreatment" is used to refer mainly to treating biomass in some way prior to enzymatic hydrolysis in order to improve the yield of sugars. This pretreatment may be chemical, such as with dilute acid, thermochemical, such as with dilute acid and elevated temperature, or other methods like ammonia fiber explosion (AFEX: <http://www.springerlink.com/content/phng830883117843/>) . As explained earlier, biomass is pretreated in an attempt to fragment mainly lignin and to better expose cellulose and hemicellulose to enzymatic action.

Thermochemical Technologies

Thermochemical conversion technologies typically involve two main steps: gasification and subsequent catalytic conversion of the resultant synthesis gas to liquid fuels such as ethanol. This process is sometimes referred to as Fischer-Tropsch (http://www1.eere.energy.gov/biomass/catalytic_conversion.html#background), or gas-to-liquid (GTL) technology. A comprehensive description of this general process is provided by Spath and Dayton, 2003 (<http://www1.eere.energy.gov/biomass/pdfs/34929.pdf>) . In addition, SASOL in South Africa has been using the process to produce gasoline from coal for several decades (http://www.sasol.com/sasol_internet/frontend/navigation.jsp?navid=1600033&rootid=2 and http://www1.eere.energy.gov/biomass/catalytic_conversion.html#background).

Gasification

Products of regular combustion of biomass, such as occurs in a campfire, are water vapor (H_2O), carbon dioxide (CO_2) and ash. Gasification is partial combustion which takes place in a gasifier where the amount of air (and therefore, oxygen) that enters the reaction is restricted. With limited oxygen, instead of H_2O being released, only hydrogen (H_2) is produced, and instead of only carbon dioxide (CO_2), carbon monoxide (CO) is also produced. Along with other minor constituents like methane (CH_4), these gases are known as synthesis gas, or syngas (in some older texts the term producer gas is used).

Catalytic Conversion

The relative amount of different component gases in syngas will be influenced by the composition of the feedstock, conditions in the gasifier, such as temperature and pressure, and other factors like introduction of steam to the gasifier, which is often referred to as steam reforming. In turn, the relative amounts of different gases in the syngas will impact the amount of liquid fuel obtained in the catalytic conversion step. Following gasification, syngas needs to be cleaned up before passing it across a catalyst in a catalytic reactor in order to ensure that the catalyst is not contaminated or poisoned (http://www1.eere.energy.gov/biomass/gas_cleanup.html).

Catalysts that can produce liquid fuels from syngas typically include elements such as zinc, chromium, cobalt, copper and molybdenum. Each is specifically selective for certain liquid fuels, and sensitive to different contaminants and poisons. The exact composition of the catalyst is often a proprietary feature of variations in this technology owned by different companies. Typically, these chemical catalysts produce a mixture of alcohols which may need to be separated by fractionation. The proportion of different alcohols and yield of alcohol per ton of biomass is dependent on composition of the feedstock, and therefore, composition of syngas, as well as conditions in the catalytic reactor, such as heat and pressure. Catalytic reactors often need to be operated at relatively high heat and pressure, which results in high capital costs for equipment.

Another variation of the thermochemical process is use of microorganisms to convert or ferment the syngas to ethanol. In contrast to chemical catalytic conversion, this process can produce pure ethanol as opposed to a mixture of alcohols (<http://www1.eere.energy.gov/biomass/pdfs/34929.pdf> and http://www1.eere.energy.gov/biomass/synthesis_gas_fermentation.html).

CELLULOSIC HYDROCARBON FUEL TECHNOLOGIES

Cellulosic hydrocarbon fuels include cellulosic diesel, gasoline and aviation fuel. These fuels are often referred to as synthetic fuels because they are produced by synthesis of small molecules such as hydrogen and carbon monoxide in the synthesis gas or syngas from a gasifier, into larger ones. However, for the purpose of this document the terms “cellulosic hydrocarbons” and “cellulosic diesel, gasoline and aviation fuel” are preferred because this indicates clearly that the raw material from which these fuels are produced is cellulosic biomass and not fossil fuels.

Gasification and catalytic conversion

One procedure for producing cellulosic hydrocarbon fuels is gasification and catalytic conversion, as described above for production of cellulosic ethanol, but with different catalysts.

Depolymerization and catalytic synthesis

Depolymerization and catalytic synthesis involves various technologies to first reduce particle size physically as much as possible. This is then followed by moderate temperature thermal depolymerization (not gasification) of this material and catalytic cracking, and finally, by catalytic synthesis of the resultant molecules into liquid fuels. While this process is not well known in the emerging cellulosic biofuel industry, components of it are well established in the chemical manufacturing and oil refining industries. Therefore, the process offers several distinct advantages such as off-the-shelf equipment and continuous rather than batch processing, which facilitate relatively low capital costs.

COMPARATIVE ANALYSIS

In this section, based on literature and web surveys, visits to companies, and interviews with individuals, an attempt is made to assess the different cellulosic biofuel technologies on the basis of several criteria: yield of biofuel per ton of biomass, size and capital costs of processing plants, production cost/gal, and relationship with other industries.

Biofuel yield per ton of biomass.

Of utmost importance in determining production costs is yield of biofuel per ton of biomass. In this regard, the maximum potential yield of cellulosic ethanol with thermochemical conversion is almost double that for biochemical conversion. For example, the theoretical maximum yield of ethanol from switchgrass is 111 gal/ton of biomass for the biochemical process, and 198.4 gal/ton, or 56% more for the thermochemical process (Appendix A). In reality, the projections made by companies

developing the technologies for current capability were about 65 and 100 gal/ton for the biochemical and thermochemical processes, respectively, although some projections are as high as 200 gal/to for the thermochemical process. The lower efficiency for the biochemical process is at least partly due to the fact that this technology cannot make use of the lignin, whereas the thermochemical process does. The biochemical processes also release CO₂ during the fermentation stage, while there is no similar loss from the catalytic reactor used in the thermochemical processes. Yield predictions for the depolymerization and catalytic synthesis of cellulosic hydrocarbon biofuels are around 200 gal/ton, which would place this process in the lead within this category.

Size and capital costs of processing plants

The general impression from the literature is that processing plants are very sensitive to economies of scale, and therefore need to be large (50+ million gallons per year). However, there were companies developing both biochemical and thermochemical processes that determined that relatively small plants (less than 20 million gallons per year) were profitable. Some were proposing plants as small as a million gallons per year. Projected capital costs for all cellulosic ethanol technologies were mostly \$2 to \$6 per annual gallon, which is considerably more than the \$1.30 - \$1.50 per annual gallon required to build corn-to-ethanol plants.

In contrast, projected capital costs for the depolymerization and catalytic synthesis of cellulosic hydrocarbon biofuels are well under a dollar per gallon, even for relatively small plants. As indicated earlier, part of the reason for this is the ability to use off-the-shelf equipment from the chemical manufacturing industries, and use of continuous instead of batch processing. Consequently, this technology is well below all others in capital cost.

Production cost per gallon

Companies developing the thermochemical process mostly expected production cost per gallon to be around \$1.00, depending on feedstock cost. The equivalent cost for the biochemical process was projected to be about \$2.00 per gallon. It is likely that the difference in processing costs between the two technologies is due primarily to the associated difference in yield of ethanol per ton. Projected cost per gallon of cellulosic hydrocarbon fuels produced by depolymerization and catalytic synthesis is well below a dollar per gallon, mainly because of high efficiency and low capital costs.

Relationship to other industries

The biochemical process has many similarities with the pulp and paper, sugarcane processing and corn-to ethanol industries, while the thermochemical and depolymerization and catalytic synthesis processes are more closely aligned with the oil refining and chemical manufacturing industries.

PROGRESS TOWARDS COMMERCIALIZATION

Progress towards commercialization is indicated by listing companies that are attempting to commercialize different conversion processes and technologies, along with their contact information. Companies involved in enzyme development for enzymatic hydrolysis and fermentation are also listed. However, this is not an exhaustive list, as several companies chose to not be included.

Cellulosic Ethanol

Dilute acid hydrolysis and fermentation

SEKAB: <http://www.sekab.com>

Concentrated acid hydrolysis and fermentation

Arkenol: <http://www.arkenol.com/>

Brelsford Engineering: <http://www.beienginc.com/>

Masada Resource Group: <http://www.eba-nys.org/eba/971q/8masada.html>

Enzymatic hydrolysis and fermentation

Abengoa Bioenergy: <http://www.abengoabioenergy.com>

Biofuels Energy Corporation: www.biofuelsenergycorp.com

Iogen: www.iogen.ca

Mascoma: www.mascoma.com

Verenium: <http://www.verenium.com/index.html>

Enzyme production

Diversa: www.diversa.com

Dyadic: www.dyadic-group.com/

Novozymes: www.novozymes.com

Verenium: <http://www.verenium.com/index.html>

Gasification and catalytic conversion

Bioconversion Technologies LLC - <http://www.bio-conversiontechnologies.com>)

Range Fuels: www.rangefuels.com

Pearson Technologies:

<http://saubr.ua.edu/saubrpresentations/Bruce%20Vantine.pdf>

Syntec Biofuels/NetCo: www.syntecbiofuel.com/ and <http://www.sys-con.com/read/204863.htm>)

Woodland Chemical Systems: www.woodlandchemicals.com

Bioengineering Resources:

http://thefraserdomain.typepad.com/energy/2005/12/synthesis_gas_f.html

Cellulosic Hydrocarbon Fuels

Gasification and catalytic conversion

Rentech Inc.: <http://www.rentechinc.com/>

Choren Industries: www.choren.com

Depolymerization and catalytic synthesis

BIOeCON: www.bio-e-con.com

CONCLUSIONS

This document summarizes information obtained in a survey of cellulosic biofuel technologies. The main limitations of the report are 1) the fact that a considerable amount of information is owned by private companies that, for obvious reasons, would not allow it to be released, 2) cellulosic biofuel production is a very rapidly emerging industry, with new technologies and companies appearing every few weeks, and 3) the fact that the analysis took into account only biofuel production, and not production of co-products.

In view of these limitations, those interested in learning more about the industry are encouraged to contact the companies listed above directly, and to keep up to date as the industry develops. Furthermore, while doing this, great emphasis should be placed on the ability of technologies to produce multiple products, as indicated for the oil industry below. It should be recognized that while most of the attention within the field of cellulosic biofuels is focused on cellulosic ethanol, cellulosic hydrocarbon biofuels offer considerable advantages over this option and could be the first to enter the commercial market. Based on this review, it appears likely that the first commercial scale cellulosic biofuel plant in the United States will be in production by 2009, and this could mark the point where the country starts moving from a fossil fuel based economy to a cellulose based economy.

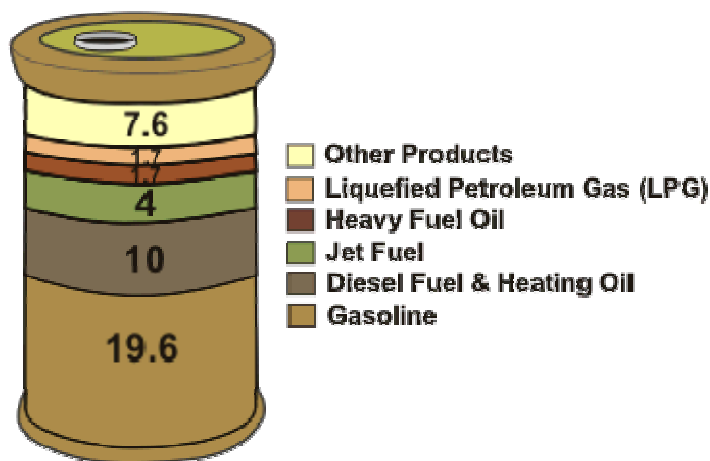


Figure 13. Gallons of products derived from a 42-gallon barrel of oil.

(Source: <http://www.eia.doe.gov/neic/brochure/gas04/gasoline.htm>)

APPENDIX A



NREL National Renewable Energy Laboratory

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

Innovation for Our Energy Future

Technical Memorandum

To: National Bioenergy Center

Title: Maximum Yield of Liquid Fuels from Biomass Based on Stoichiometry

Author: John Jechura

Platform: Analysis, Biochemical, Thermochemical

Date: July 17, 2006

Abstract: Biomass must be chemically converted for production of liquid fuels, not just to convert it from a solid to a liquid but also to add hydrogen and reject excess oxygen. In this technical note the overall chemistry for the conversion is used to determine the maximum amount of fuel that can be made from biomass and how much water is consumed. The formation of carbon dioxide is necessary to reject excess oxygen but it carries very little energy penalty. Even though a significant mass of the feedstock is rejected (as much as 60% depending upon the fuel produced) the energy content of the produced fuel is essentially that of the converted biomass. The biomass conversion process can be thought of as an energy densification process.

Keywords: Biochemical Analysis, Thermochemical Analysis

Biomass must be chemically converted for production of liquid fuels. Obvious changes are necessary to convert biomass from a solid to a liquid. Less obvious is the chemical nature of biomass vs. the desired fuels – biomass generally has too little hydrogen (which must be added), too much oxygen (which must be rejected), and other undesirable elements (such as nitrogen and sulfur) which also must be rejected.

Two questions are often asked about this biomass conversion:

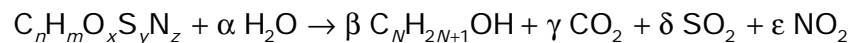
- What is the maximum amount of fuel that can be made from biomass? This is usually expressed as volume per unit mass (such as gallons per ton) or on an energy equivalency basis (heating value of the fuel vs. the heating value of the starting biomass).
- How much water is consumed in this conversion? This will usually be expressed as volume per unit volume of fuel produced (such as gallons per gallon).

In this technical note we'll examine the maximum fuel production based upon the overall chemistry for the conversion. The following are considerations for developing the model chemical reaction from which the calculations will be based:

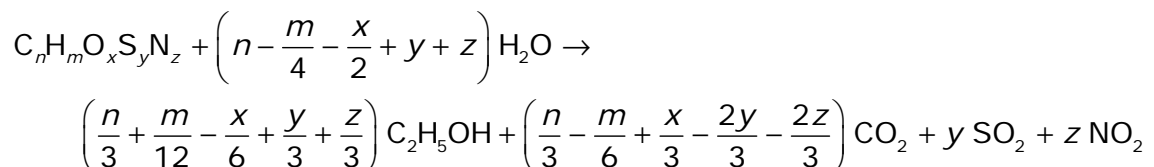
- *Hydrogen addition.* In this model chemical reaction hydrogen will be introduced as water. There is a disadvantage in that this also adds extra oxygen which must be rejected. From a yield stand point, it would be most desirable to add hydrogen in its diatomic form (H_2). However, hydrogen is generally produced via reforming of natural gas and this would introduce a non-renewable feedstock for biomass conversion. For this reason direct addition as H_2 will not be considered for the model chemical reaction.
- *Oxygen rejection.* It would be most desirable to reject the excess oxygen in diatomic form (O_2). However, this is not a likely form based upon typical conversion pathways. The most undesirable way to reject oxygen is as water – we generally need to add hydrogen to make the fuel, so this just removes the hydrogen added. Rejecting as carbon monoxide (CO) is not desirable since every mole of oxygen also removes a mole of carbon that should go to the end-product fuel; this is also undesirable since CO has an energy content in terms of its heating value. Rejecting as carbon dioxide (CO_2) is acceptable since every mole of oxygen removes only half a mole of carbon; in addition CO_2 has zero energy content in terms of its heating value.
- *Rejection of other undesired elements.* The sulfur and nitrogen will also be rejected in the oxide form. This is analogous to the combustion pathway. These oxides have no heating value similar to CO_2 . These oxides do play a positive role in rejecting excess oxygen, reducing the loss of the biomass's carbon.

We'll work with an average biomass molecule, $C_nH_mO_xS_yN_z$, where the atom numbers n , m , x , y , and z are determined from the elemental analysis. Two different types of liquid fuels will be considered:

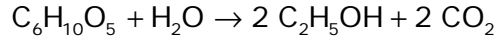
- *N-carbon alcohols.* The model chemical reaction producing an N-carbon alcohol as the liquid fuel is:



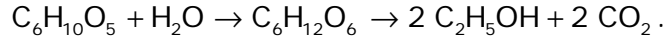
where α , β , γ , δ , and ε are stoichiometric coefficients. These stoichiometric coefficients can be determined from the linear equations arising from the atom balances (see Appendix A). For example, the overall reaction for making ethanol ($N = 2$) is:



A more specific example is the hydrolysis of cellulose to glucose followed by fermentation of glucose to ethanol. Using the monomeric unit of cellulose as the basis for the average biomass molecule, the overall chemical reaction is:

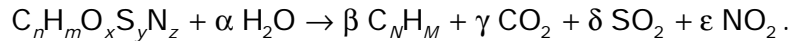


This is typically written in two steps to formally show the pathway with the glucose formation specifically noted:

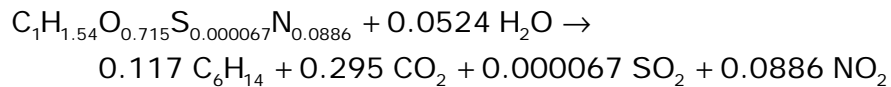


Note that this overall reaction is not conversion pathway specific – it is just as valid for thermochemical conversions as it is for biochemical conversions. The difference for thermochemical conversions is that the intermediate species are syngas components instead of sugars.

- *Hydrocarbons.* Conversion of biomass to hydrocarbons via syngas and Fischer-Tropsch catalysts is very well known¹. Aqueous phase conversion pathways have also been reported that convert biomass directly to a hydrocarbon (such as by Dumesic and co-workers^{2,3}); the generalized formula for this overall reaction would be:



Again, these stoichiometric coefficients can be determined from the atom balances (again see Appendix A). As an example, if we consider making only hexane from corn stover then the overall reaction is:



where the atom numbers have been normalized on the basis of one carbon atom in the average corn stover molecule.

The desired numeric values can be calculated from the balanced overall chemical reaction:

- Mass of biomass can be derived from the moles of the average biomass molecule using the molecular weight.
- Volume of the fuel and water can be derived using the molecular weight and the standard liquid density^a of the species.

^a The standard conditions for liquid density in the U.S. is 60°F and 1 atm. However, if the liquid is volatile then the pressure is the bubble point pressure of the liquid at 60°F.

Table 1 summarizes the maximum fuel yield and water consumption at this maximum fuel yield for three types of biomass (corn stover⁴, switch grass⁵, and wood⁶) and five biomass constituents (lignin⁴, C5 and C6 polysaccharides, and C5 and C6 sugars). Four fuels are considered, two alcohols (ethanol and n-butanol) and two hydrocarbons (n-hexane and benzene). The detailed tables are shown in Appendix B.

Table 1. Maximum Ethanol Yield & Associated Water Consumption Based on Stoichiometry

| | Corn Stover | Switch Grass | Wood | Corn Stover Lignin | C6 Sugar | C6 Poly-saccharide | C5 Sugar | C5 Poly-saccharide |
|--|-------------|--------------|--------|--------------------|----------|--------------------|----------|--------------------|
| Biomass Info | | | | | | | | |
| <i>Mass Distributions (dry & ash free)</i> | | | | | | | | |
| Carbon | 47.80 | 49.4 | 51.35 | 77.5 | 40.0 | 44.4 | 40.0 | 45.5 |
| Hydrogen | 6.16 | 6.11 | 6.10 | 9.0 | 6.7 | 6.2 | 6.7 | 6.1 |
| Oxygen | 45.54 | 44 | 42.29 | 13.4 | 53.3 | 49.3 | 53.3 | 48.4 |
| Sulfur | 0.01 | 0.12 | 0.09 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Nitrogen | 4.94 | 0.64 | 0.17 | 0.0 | 15.5 | 14.4 | 18.7 | 17.0 |
| HHV (Btu/lb) | 8,056 | 8,241 | 8,422 | 16,431 | 6,724 | 7,464 | 6,732 | 7,638 |
| Ethanol Production | | | | | | | | |
| Mass (ton/ton) | 0.652 | 0.659 | 0.688 | 1.271 | 0.511 | 0.568 | 0.511 | 0.581 |
| Volume (gal/ton) | 196.4 | 198.4 | 207.2 | 382.7 | 154.0 | 171.1 | 154.0 | 175.0 |
| Efficiency | | | | | | | | |
| lb/lb | 0.652 | 0.659 | 0.688 | 1.271 | 0.511 | 0.568 | 0.511 | 0.581 |
| Btu/Btu | 1.034 | 1.020 | 1.043 | 0.987 | 0.971 | 0.972 | 0.970 | 0.971 |
| Water Consumption | | | | | | | | |
| gal/ton feedstock | 57.1 | 54.8 | 63.0 | 163.9 | 0.0 | 26.7 | 0.0 | 32.7 |
| gal/gal fuel | 0.291 | 0.276 | 0.304 | 0.428 | 0.000 | 0.156 | 0.000 | 0.187 |
| Butanol Production | | | | | | | | |
| Mass (ton/ton) | 0.525 | 0.530 | 0.554 | 1.023 | 0.411 | 0.457 | 0.411 | 0.468 |
| Volume (gal/ton) | 154.5 | 156.1 | 163.0 | 301.2 | 121.2 | 134.6 | 121.2 | 137.7 |
| Efficiency (Btu/Btu) | | | | | | | | |
| lb/lb | 0.525 | 0.530 | 0.554 | 1.023 | 0.411 | 0.457 | 0.411 | 0.468 |
| Btu/Btu | 1.011 | 0.998 | 1.020 | 0.966 | 0.950 | 0.951 | 0.949 | 0.950 |
| Water Consumption | | | | | | | | |
| gal/ton feedstock | 26.5 | 23.9 | 30.7 | 104.3 | -24.0 | 0.0 | -24.0 | 5.5 |
| gal/gal fuel | 0.172 | 0.153 | 0.188 | 0.346 | -0.198 | 0.000 | -0.198 | 0.040 |
| Hexane Production | | | | | | | | |
| Mass (ton/ton) | 0.385 | 0.389 | 0.406 | 0.751 | 0.302 | 0.336 | 0.302 | 0.343 |
| Volume (gal/ton) | 139.3 | 140.7 | 146.9 | 271.4 | 109.2 | 121.3 | 109.2 | 124.1 |
| Efficiency (Btu/Btu) | | | | | | | | |
| lb/lb | 0.385 | 0.389 | 0.406 | 0.751 | 0.302 | 0.336 | 0.302 | 0.343 |
| Btu/Btu | 0.994 | 0.981 | 1.002 | 0.949 | 0.933 | 0.934 | 0.932 | 0.934 |
| Water Consumption | | | | | | | | |
| gal/ton feedstock | 8.8 | 6.0 | 12.0 | 69.7 | -37.9 | -15.4 | -37.9 | -10.3 |
| gal/gal fuel | 0.063 | 0.043 | 0.082 | 0.257 | -0.347 | -0.127 | -0.347 | -0.083 |
| Benzene Production | | | | | | | | |
| Mass (ton/ton) | 0.442 | 0.447 | 0.467 | 0.862 | 0.347 | 0.385 | 0.347 | 0.394 |
| Volume (gal/ton) | 120.2 | 121.4 | 126.8 | 234.3 | 94.2 | 104.7 | 94.2 | 107.1 |
| Efficiency (Btu/Btu) | | | | | | | | |
| lb/lb | 0.442 | 0.447 | 0.467 | 0.862 | 0.347 | 0.385 | 0.347 | 0.394 |
| Btu/Btu | 0.988 | 0.975 | 0.997 | 0.944 | 0.928 | 0.929 | 0.927 | 0.928 |
| Water Consumption | | | | | | | | |
| gal/ton feedstock | -53.0 | -56.5 | -53.2 | -50.8 | -86.4 | -69.3 | -86.4 | -65.4 |
| gal/gal fuel | -0.441 | -0.465 | -0.420 | -0.217 | -0.916 | -0.662 | -0.916 | -0.611 |

There is a wealth of information from these results:

- The maximum yields are the greatest for those constituents that have the lowest oxygen content, such as lignin.

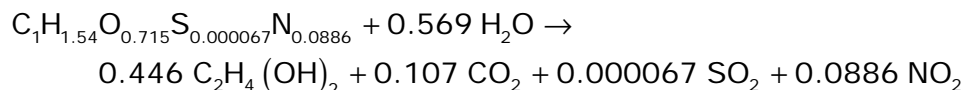
- The three types of biomass all have nearly the same oxygen contents (42 to 46%) and will have very similar maximum fuel yields (about 200 gallons ethanol per ton, 155 to 160 gallons butanol per ton, etc.).
- The amount of water consumed is highly dependent on the type of fuel being produced. Ethanol requires about 0.3 gal/gal, but hexane requires almost no water, and benzene actually creates water (as implied from the negative values for water consumption).
- The energy efficiencies (as defined as the ratio of the heating value of the produced fuel to the heating value of the feedstock) are all very nearly one. This means that even though a significant mass of the feedstock is rejected (as much as 60% depending upon the fuel produced) there is little penalty on the energy content of the produced fuel. The biomass conversion operation can be thought of as a way to concentrate the biomass potential energy in a more energy dense form.

The results in Table 1 imply that one or more conversion pathways will be used that can convert all of the biomass as desired. This may be an appropriate assumption for a Thermochemical conversion pathway such as using a syngas intermediate. However, current Biochemical pathways, such as fermentation to ethanol, are limited to the conversion of the C6 and C5 polysaccharides and sugars via hydrolysis and fermentation. When dealing with a specific conversion pathway this must be taken into account. Table 2 shows the maximum ethanol yield taking into account that only the carbohydrate portion can be converted.

Table 2. Maximum Ethanol Yield Via Fermentation Pathway

| | Mass Fractions | | Maximum Ethanol Yield (gal/ton) |
|---------------------------|--------------------|--------------------|---------------------------------|
| | C6 Polysaccharides | C5 Polysaccharides | |
| Corn Stover ⁷ | 40.9 | 24.0 | 112 |
| Switch Grass ⁸ | 51.0 | 13.3 | 111 |

Even though the energy content of the fuel is essentially that of the original biomass, a great deal of the mass is lost due to the carbon dioxide formation (and oxygen rejection). There may be some desire to retain as much of the mass as possible. One way to do this is to try to convert the biomass to a material that has more than one oxygen atom per molecule, for example, ethylene glycol. The balanced chemical reaction at maximum yield for this is:



This reaction indicates that the maximum mass yield of glycol is 106% of the original biomass (mass increases because of the added water) and the volumetric yield is 228 gal/ton. The energy efficiency is 1.08 Btu/Btu, just a little higher than that possible for ethanol. So, even though more of mass is utilized, there is very little energy advantage to making a product with more oxygen.

The observations can be summarized as:

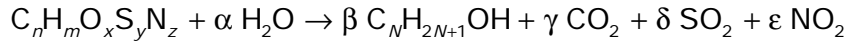
- The different types of biomass have very similar liquid fuel yields because the compositions are very similar.
- Maximum fuel yields are constrained by the stoichiometry of the conversion process. The formation and rejection of CO₂ is necessary to reject excess oxygen from the biomass feedstock.
- The formation and rejection of CO₂ carries very little energy penalty at maximum fuel yields.
- Even though a great deal of the original feedstock's mass may be rejected the final fuel may still have nearly all of the energy of the original feedstock.
- The amount of water consumed in the biomass conversion process is highly dependent upon the type of fuel produced. If the fuel a very low hydrogen content (such as for an aromatic like benzene) it is possible that water would be created and not consumed.

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- ⁸ Mean value for switch grass from Phyllis database, June 6, 2006.
<http://www.ecn.nl/phyllis/>

Appendix A – Determination of Stoichiometric Coefficients

Focusing on the carbon, hydrogen, oxygen, sulfur, and nitrogen content of the biomass, the generalized formula for producing an N-carbon alcohol as the liquid fuel is:



where the excess oxygen is rejected with the undesired sulfur and nitrogen but also with some of the desired carbon. The stoichiometric coefficients can be determined from the linear equations arising from the atom balances. For this reaction:

$$\text{Carbon:} \quad n = \beta \cdot N + \gamma$$

$$\text{Hydrogen:} \quad m + 2 \cdot \alpha = \beta \cdot (2N + 2) + \gamma$$

$$\text{Oxygen:} \quad x + \alpha = \beta + 2 \cdot \gamma + 2 \cdot \delta + 2 \cdot \varepsilon$$

$$\text{Sulfur:} \quad y = \delta$$

$$\text{Nitrogen:} \quad z = \varepsilon$$

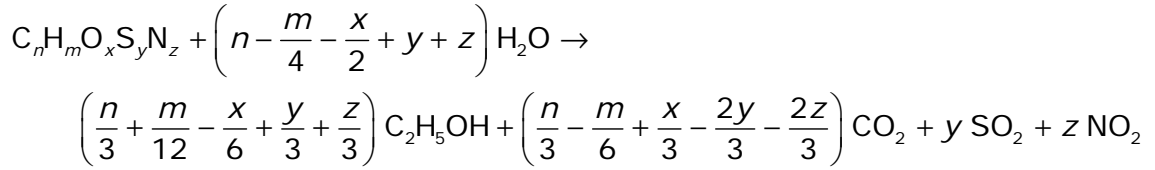
The stoichiometric for sulfur and nitrogen are obvious, but the others are interrelated. These linear equations and the solution for the stoichiometric coefficients can be expressed in matrix notation:

$$\begin{bmatrix} 0 & N & 1 & 0 & 0 \\ -2 & 2N+2 & 0 & 0 & 0 \\ -1 & 1 & 2 & 2 & 2 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \varepsilon \end{bmatrix} = \begin{bmatrix} n \\ m \\ x \\ y \\ z \end{bmatrix} \Rightarrow \begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \varepsilon \end{bmatrix} = \frac{1}{6N} \begin{bmatrix} 4N+4 & 1-2N & -(2N+2) & 4N+4 & 4N+4 \\ 4 & 1 & -2 & 4 & 4 \\ 2N & -N & 2N & -4N & -4N \\ 0 & 0 & 0 & 6N & 0 \\ 0 & 0 & 0 & 0 & 6N \end{bmatrix} \begin{bmatrix} n \\ m \\ x \\ y \\ z \end{bmatrix}.$$

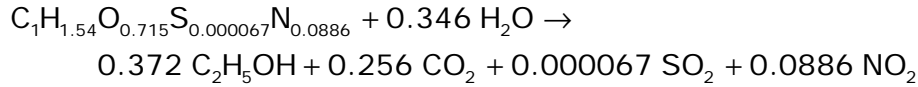
Numeric values for the stoichiometric coefficients can be easily shown using the solution equations. For example, for ethanol, $N = 2$:

$$\begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \varepsilon \end{bmatrix} = \begin{bmatrix} 1 & -\frac{1}{4} & -\frac{1}{2} & 1 & 1 \\ \frac{1}{3} & \frac{1}{12} & -\frac{1}{6} & \frac{1}{3} & \frac{1}{3} \\ \frac{1}{3} & -\frac{1}{6} & \frac{1}{3} & -\frac{2}{3} & -\frac{2}{3} \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} n \\ m \\ x \\ y \\ z \end{bmatrix}$$

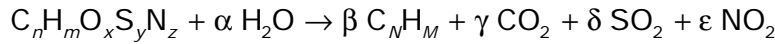
which gives the balanced chemical equation:



As a further example, for a specific biomass with atomic numbers normalized on carbon content, $n = 1$, $m = 1.54$, $x = 0.715$, $y = 0.000067$, and $z = 0.0886$, then the balanced chemical equation is:



We have also looked at the conversion biomass directly to a hydrocarbon. The generalized formula for this overall reaction would be:



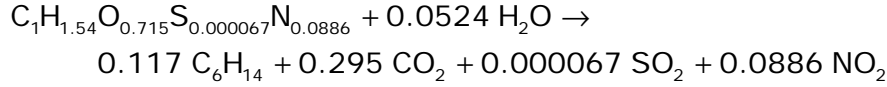
Where, again, α , β , and γ are stoichiometric coefficients. This time the atom balances give rise to the following set of linear equations:

$$\begin{bmatrix} 0 & N & 1 & 0 & 0 \\ -2 & M & 0 & 0 & 0 \\ -1 & 0 & 2 & 2 & 2 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \varepsilon \end{bmatrix} = \begin{bmatrix} n \\ m \\ x \\ y \\ z \end{bmatrix} \Rightarrow \begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \varepsilon \end{bmatrix} = \frac{1}{4N+M} \begin{bmatrix} 2M & -2N & -M & 2M & 2M \\ 4 & 1 & -2 & 4 & 4 \\ M & -N & 2N & -4N & -4N \\ 0 & 0 & 0 & 4N+M & 0 \\ 0 & 0 & 0 & 0 & 4N+M \end{bmatrix} \begin{bmatrix} n \\ m \\ x \\ y \\ z \end{bmatrix}$$

Note for a saturated hydrocarbon, such as hexane, $N = 6$ and $M = 14$, then:

$$\begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \varepsilon \end{bmatrix} = \begin{bmatrix} \frac{14}{19} & -\frac{6}{19} & -\frac{7}{19} & \frac{14}{19} & \frac{14}{19} \\ \frac{2}{19} & \frac{1}{38} & -\frac{1}{19} & \frac{2}{19} & \frac{2}{19} \\ \frac{7}{19} & -\frac{3}{19} & \frac{6}{19} & -\frac{12}{19} & -\frac{12}{19} \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} n \\ m \\ x \\ y \\ z \end{bmatrix}$$

and for our sample biomass the balanced chemical equation is:



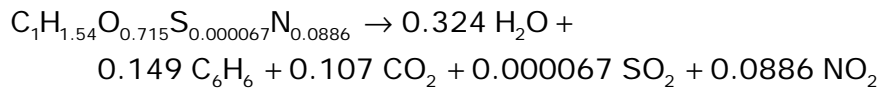
For an unsaturated hydrocarbon, such as benzene, $N = M = 6$, then:

$$\begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \epsilon \end{bmatrix} = \begin{bmatrix} \frac{2}{5} & -\frac{2}{5} & -\frac{1}{5} & \frac{2}{5} & \frac{2}{5} \\ \frac{2}{15} & \frac{1}{30} & -\frac{1}{15} & \frac{2}{15} & \frac{2}{15} \\ \frac{1}{5} & -\frac{1}{5} & \frac{2}{5} & -\frac{4}{5} & -\frac{4}{5} \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} n \\ m \\ x \\ y \\ z \end{bmatrix}.$$

For our sample biomass the result for benzene is different from what we've already seen above. The values from the linear equations are:

$$\begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \delta \\ \epsilon \end{bmatrix} = \begin{bmatrix} \frac{2}{5} & -\frac{2}{5} & -\frac{1}{5} & \frac{2}{5} & \frac{2}{5} \\ \frac{2}{15} & \frac{1}{30} & -\frac{1}{15} & \frac{2}{15} & \frac{2}{15} \\ \frac{1}{5} & -\frac{1}{5} & \frac{2}{5} & -\frac{4}{5} & -\frac{4}{5} \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 1.54 \\ 0.715 \\ 0.000067 \\ 0.0886 \end{bmatrix} = \begin{bmatrix} -0.324 \\ 0.149 \\ 0.107 \\ 0.000067 \\ 0.0886 \end{bmatrix}.$$

Since the stoichiometric coefficient for water is negative then, overall, *water is being produced, not consumed*. So, for this specific biomass the balanced chemical equation for hexane is:



Appendix B – Detailed Conversion Table

| | Corn Stover | Switch Grass | Wood | Corn Stover Lignin | C6 Sugar | C6 Poly- saccharide | C5 Sugar | C5 Poly- saccharide |
|--|----------------|-----------------|--------|--------------------------|----------|------------------------|----------|------------------------|
| Biomass Info | | | | | | | | |
| <i>Mass Distributions (dry & ash free)</i> | | | | | | | | |
| Carbon | 47.80 | 49.4 | 51.35 | 77.5 | 40.0 | 44.4 | 40.0 | 45.5 |
| Hydrogen | 6.16 | 6.11 | 6.10 | 9.0 | 6.7 | 6.2 | 6.7 | 6.1 |
| Oxygen | 45.54 | 44 | 42.29 | 13.4 | 53.3 | 49.3 | 53.3 | 48.4 |
| Sulfur | 0.01 | 0.12 | 0.09 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Nitrogen | 4.94 | 0.64 | 0.17 | 0.0 | 15.5 | 14.4 | 18.7 | 17.0 |
| <i>Atom Numbers</i> | | | | | | | | |
| Carbon | 3.98 | 4.11 | 4.28 | 10 | 6 | 6 | 5 | 5 |
| Hydrogen | 6.11 | 6.06 | 6.05 | 13.9 | 12 | 10 | 10 | 8 |
| Oxygen | 2.85 | 2.75 | 2.64 | 1.3 | 6 | 5 | 5 | 4 |
| Sulfur | 0.00027 | 0.0037 | 0.0028 | 0 | 0 | 0 | 0 | 0 |
| Nitrogen | 0.353 | 0.046 | 0.012 | 0 | 0 | 0 | 0 | 0 |
| HHV (Btu/lb) | 8,056 | 8,241 | 8,422 | 16,431 | 6,724 | 7,464 | 6,732 | 7,638 |
| Ethanol Production | | | | | | | | |
| <i>Moles</i> | | | | | | | | |
| H2O | 1.381 | 1.272 | 1.457 | 5.875 | 0.000 | 1.000 | 0.000 | 1.000 |
| C2H5OH | 1.479 | 1.434 | 1.494 | 4.275 | 2.000 | 2.000 | 1.667 | 1.667 |
| CO2 | 1.021 | 1.244 | 1.288 | 1.450 | 2.000 | 2.000 | 1.667 | 1.667 |
| SO2 | 0.000 | 0.004 | 0.003 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NO2 | 0.353 | 0.046 | 0.012 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mass (ton/ton) | 0.652 | 0.659 | 0.688 | 1.271 | 0.511 | 0.568 | 0.511 | 0.581 |
| Volume (gal/ton) | 196.4 | 198.4 | 207.2 | 382.7 | 154.0 | 171.1 | 154.0 | 175.0 |
| <i>Efficiency</i> | | | | | | | | |
| lb/lb | 0.652 | 0.659 | 0.688 | 1.271 | 0.511 | 0.568 | 0.511 | 0.581 |
| Btu/Btu | 1.034 | 1.020 | 1.043 | 0.987 | 0.971 | 0.972 | 0.970 | 0.971 |
| <i>Water Consumption</i> | | | | | | | | |
| gal/ton feedstock | 57.1 | 54.8 | 63.0 | 163.9 | 0.0 | 26.7 | 0.0 | 32.7 |
| gal/gal fuel | 0.291 | 0.276 | 0.304 | 0.428 | 0.000 | 0.156 | 0.000 | 0.187 |
| Butanol Production | | | | | | | | |
| <i>Moles</i> | | | | | | | | |
| H2O | 0.641 | 0.555 | 0.710 | 3.738 | -1.000 | 0.000 | -0.833 | 0.167 |
| C4H9OH | 0.740 | 0.717 | 0.747 | 2.138 | 1.000 | 1.000 | 0.833 | 0.833 |
| CO2 | 1.021 | 1.244 | 1.288 | 1.450 | 2.000 | 2.000 | 1.667 | 1.667 |
| SO2 | 0.000 | 0.004 | 0.003 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NO2 | 0.353 | 0.046 | 0.012 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mass (ton/ton) | 0.525 | 0.530 | 0.554 | 1.023 | 0.411 | 0.457 | 0.411 | 0.468 |
| Volume (gal/ton) | 154.5 | 156.1 | 163.0 | 301.2 | 121.2 | 134.6 | 121.2 | 137.7 |
| <i>Efficiency (Btu/Btu)</i> | | | | | | | | |
| lb/lb | 0.525 | 0.530 | 0.554 | 1.023 | 0.411 | 0.457 | 0.411 | 0.468 |
| Btu/Btu | 1.011 | 0.998 | 1.020 | 0.966 | 0.950 | 0.951 | 0.949 | 0.950 |
| <i>Water Consumption</i> | | | | | | | | |
| gal/ton feedstock | 26.5 | 23.9 | 30.7 | 104.3 | -24.0 | 0.0 | -24.0 | 5.5 |
| gal/gal fuel | 0.172 | 0.153 | 0.188 | 0.346 | -0.198 | 0.000 | -0.198 | 0.040 |
| Hexane Production | | | | | | | | |
| <i>Moles</i> | | | | | | | | |
| H2O | 0.213 | 0.139 | 0.278 | 2.500 | -1.579 | -0.579 | -1.316 | -0.316 |
| C6H14 | 0.467 | 0.453 | 0.472 | 1.350 | 0.632 | 0.632 | 0.526 | 0.526 |
| CO2 | 1.177 | 1.395 | 1.445 | 1.900 | 2.211 | 2.211 | 1.842 | 1.842 |
| SO2 | 0.000 | 0.004 | 0.003 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NO2 | 0.353 | 0.046 | 0.012 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mass (ton/ton) | 0.385 | 0.389 | 0.406 | 0.751 | 0.302 | 0.336 | 0.302 | 0.343 |
| Volume (gal/ton) | 139.3 | 140.7 | 146.9 | 271.4 | 109.2 | 121.3 | 109.2 | 124.1 |
| <i>Efficiency (Btu/Btu)</i> | | | | | | | | |
| lb/lb | 0.385 | 0.389 | 0.406 | 0.751 | 0.302 | 0.336 | 0.302 | 0.343 |
| Btu/Btu | 0.994 | 0.981 | 1.002 | 0.949 | 0.933 | 0.934 | 0.932 | 0.934 |
| <i>Water Consumption</i> | | | | | | | | |
| gal/ton feedstock | 8.8 | 6.0 | 12.0 | 69.7 | -37.9 | -15.4 | -37.9 | -10.3 |
| gal/gal fuel | 0.063 | 0.043 | 0.082 | 0.257 | -0.347 | -0.127 | -0.347 | -0.083 |
| Benzene Production | | | | | | | | |
| <i>Moles</i> | | | | | | | | |
| H2O | -1.282 | -1.310 | -1.232 | -1.820 | -3.600 | -2.600 | -3.000 | -2.000 |
| C6H14 | 0.592 | 0.574 | 0.597 | 1.710 | 0.800 | 0.800 | 0.667 | 0.667 |
| CO2 | 0.429 | 0.671 | 0.691 | -0.260 | 1.200 | 1.200 | 1.000 | 1.000 |
| SO2 | 0.000 | 0.004 | 0.003 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NO2 | 0.353 | 0.046 | 0.012 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mass (ton/ton) | 0.442 | 0.447 | 0.467 | 0.862 | 0.347 | 0.385 | 0.347 | 0.394 |
| Volume (gal/ton) | 120.2 | 121.4 | 126.8 | 234.3 | 94.2 | 104.7 | 94.2 | 107.1 |
| <i>Efficiency (Btu/Btu)</i> | | | | | | | | |
| lb/lb | 0.442 | 0.447 | 0.467 | 0.862 | 0.347 | 0.385 | 0.347 | 0.394 |
| Btu/Btu | 0.988 | 0.975 | 0.997 | 0.944 | 0.928 | 0.929 | 0.927 | 0.928 |
| <i>Water Consumption</i> | | | | | | | | |
| gal/ton feedstock | -53.0 | -56.5 | -53.2 | -50.8 | -86.4 | -69.3 | -86.4 | -65.4 |
| gal/gal fuel | -0.441 | -0.465 | -0.420 | -0.217 | -0.916 | -0.662 | -0.916 | -0.611 |